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(54) TITANIUM OXIDE, PHOTOCATALYST BODY FORMED BY USING IT, AND PHOTOCATALYST BODY COATING AGENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photocatalyst body exhibiting a high photocatalytic action by visible ray irradiation, and to provide a titanium oxide, which is a catalytic component, and a photocatalyst coating agent for giving a photocatalytic action to a building material, a motor vehicle material and the like.

SOLUTION: This titanium oxide has three or more peaks in the g value range from 1.930 to 2.030 in its electron spin resonance spectrum, and the maximum peak among the peaks is in the g value range from 1.990 to 2.020.

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CLAIMS

[Claim(s)]

[Claim 1] Titanium oxide characterized by the peak which has three or more peaks among the g values 1.930–2.030 in an electron-spin-resonance spectrum, and serves as the maximum of these peaks existing among the g values 1.990–2.020.

[Claim 2] The photocatalyst object characterized by including titanium oxide according to claim 1 as a catalyst component.

[Claim 3] The photocatalyst object coating agent characterized by including titanium oxide and a solvent according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to titanium oxide, the photocatalyst object which comes to use it, and a photocatalyst object coating agent. It is related with the titanium oxide as the photocatalyst object in which a high photocatalyst operation is shown by irradiating a visible ray in detail, and its catalyst component, and the photocatalyst object coating agent using it.

[0002]

[Description of the Prior Art] The electron which has a strong reduction operation when ultraviolet rays are irradiated at a semiconductor, and an electron hole with the strong oxidation generate, and a oxidation reduction operation decomposes the molecular species in contact with the semiconductor. Decomposition removal of quality of an environmental pollutant, such as decomposition removal of the malodorous substance in the decomposition, the habitation space, and the workspace of NOx in the atmosphere, mold, etc. or an underwater organic solvent, and agricultural chemicals, a surfactant, can be performed by calling such an operation photocatalyst operation and using this photocatalyst operation. Titanium oxide attracts attention as matter which has a photocatalyst operation, and the photocatalyst object which consists of titanium oxide is marketed. As commercial elegance, there is ST-01 (tradename : Ishihara Sangyo make).

[0003] However, the photocatalyst object which consists of titanium oxide marketed now was not what shows sufficient photocatalyst operation, when irradiating a visible ray.

[0004]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is by irradiating a visible ray to offer the photocatalyst object in which a high photocatalyst operation is shown, and offer the photocatalyst object coating agent for giving a photocatalyst operation further to the titanium oxide which is the catalyst component and a building material, automobile material, etc.

[0005]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of inquiring wholeheartedly, by irradiating a visible ray, this invention person etc. finds out the titanium oxide as a suitable catalyst component for the photocatalyst object in which a high photocatalyst operation is shown, and came to complete this invention.

[0006] That is, this invention offers the titanium oxide characterized by the peak which has three or more peaks among the g values 1.930-2.030 in an electron-spin-resonance spectrum, and serves as the maximum of these peaks existing among the g values 1.990-2.020.

[0007] Moreover, the photocatalyst object characterized by this invention containing the aforementioned titanium oxide as a catalyst component is offered.

[0008] Furthermore, the photocatalyst object coating agent characterized by this invention containing aforementioned titanium oxide and an aforementioned solvent is offered.

[0009]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The peak which the titanium oxide of this invention has three or more peaks among the g values 1.930-2.030 in an electron-spin-resonance (henceforth ESR) spectrum, and serves as the maximum of these peaks exists among the g values 1.990-2.020.

[0010] If ESR is divided when the energy ranking of the permanent magnetic dipole of the atom based on an unpaired electron or a molecule adds a magnetic field, and energy equal to the energy between the level is given in the form of electromagnetic energy, electromagnetic energy will be absorbed in resonance and an unpaired electron will say the thing of a phenomenon which causes changes between adjacency *****. ESR analysis investigates the direction of the crystallographic axis of the crystal containing iron family elements, and the property of a chemical bond, and is applied to investigating where [in the molecule] the unpaired electron of the free radical of an organic molecule exists. The crystal structure of titanium oxide was specified in this invention, using as an index g value calculated from ESR analysis.

[0011] With ESR equipment, g value can measure an ESR spectrum and can compute it from the position of the peak of the spectrum. The principle of ESR and the calculation method of g value are as follows [an outline]. If an unpaired electron is placed into a magnetic field, an energy level will be divided by the Zeeman effect. This disunited energy difference is set to ΔE , and it is a lower formula (I).

$$\Delta E = h\nu \quad (I)$$

h expresses a Planck's constant ($=6.6255 \times 10^{-34} \text{Js}$) among [formula (I), and ν expresses Microwave Frequency. When magnetic field strength is changed irradiating the electromagnetic field (frequency ν) of the microwave range to fill, magnetic-field-strength H is a lower formula (II).

$$h\nu = g\beta H \quad (II)$$

In the inside of [formula (II), and g, g value and β express a Bohr magneton ($=9.274 \times 10^{-24} \text{JT}^{-1}$), and H expresses flux density.] Resonance absorption happens at the time of *****, and a peak appears in the resonance absorption curve to which make a horizontal axis into magnetic field strength, and it makes a vertical axis as absorption of electromagnetic field. It is the lower formula (III) to which g value is acquired from the position of this peak as an index showing an unpaired electron's existence state, and g value is led from a formula (II).

$$g = h\nu / (\beta H) \quad (III)$$

It is alike and asks more. Usually, an ESR spectrum is expressed with the primary differential type of a resonance

absorption curve in order to raise detection sensitivity.

[0012] Although it is not clear, why titanium oxide with a specific ESR spectrum may discover the photocatalyst activity which was excellent with irradiation of a visible ray According to Journal of the Physical Chemistry, 89, and 5689-5694 (1985) From it being thought that the peak between the g values 1.930-2.030 in this ESR spectrum originates in the radical kind containing nitrogen (atomic weight 14) It is thought that distortion produced in the crystal lattice of the titanium oxide resulting from existence of nitrogen and its existence has affected the photocatalyst activity of titanium oxide.

[0013] The thing of a particle and various configurations which are fibrous is mentioned, and, as for titanium oxide, a suitable configuration is selected according to operation. Moreover, heat treatment etc. may be performed and titanium oxide may be composite-ized with an inorganic compound, after being the range which does not spoil the photocatalyst activity by irradiation of a visible ray, and mixing an inorganic compound and mixing an inorganic compound. As an inorganic compound mixed by titanium oxide, a silica (SiO_2), an alumina (aluminum 2O_3), a zirconia (ZrO_2), a magnesia (MgO), a zinc oxide (ZnO), etc. are mentioned, for example.

[0014] The titanium oxide with the specific ESR spectrum of this invention can be manufactured by the method of adding a base into the mixture of an acid and a titanium compound for example, under nitrogen-gas-atmosphere mind, and calcinating the obtained product in air etc. As an acid used at this time, a hydrochloric acid, a mineral acid like a sulfuric acid, etc. are mentioned, for example. As a titanium compound, a titanium trichloride, a titanium tetrachloride, sulfuric-acid titanium, titanyl sulfate, etc. are mentioned, for example. As a base, the matter which generates ammonia by ammonia or heating is mentioned, for example. As matter which generates ammonia, a urea, an amide compound like a formamide, an amidine compound like the acetamidine, a triethanolamine, an amine compound like a hexamethylenetetramine, etc. are mentioned, for example.

[0015] The photocatalyst object of this invention contains titanium oxide with the specific ESR spectrum mentioned above as a catalyst component.

[0016] Although this photocatalyst object consists only for example, of the aforementioned titanium oxide, what applied or covered and was able to obtain titanium oxide to the base material made of the thing of the shape of a sheet acquired by adding a forming assistant to others and particle-like titanium oxide, and carrying out extrusion molding, the thing of the shape of a sheet which was made to carry out the confounding of fibrous titanium oxide and the organic fiber, and was acquired, a metal, or a resin is mentioned. A photocatalyst object may add the inorganic oxide, a macromolecule resin, forming assistants, binders, antistatic agents, or adsorbents other than titanium oxide with the specific ESR spectrum of this invention etc. for the purpose of raising the mechanical strength and a moldability. As an inorganic oxide added by titanium oxide, a silica, an alumina, a zirconia, a magnesia, a zinc oxide, the titanium oxide in which photocatalyst activity is shown by irradiating ultraviolet rays are mentioned, for example.

[0017] What is necessary is to put a photocatalyst object, a processed liquid, or a processed gas into the glass container which penetrates a visible ray on the occasion of use of a photocatalyst object, for example, and just to irradiate the visible ray whose wavelength is 430nm or more at a photocatalyst object using the light source. It is not restricted if wavelength can irradiate a beam of light including the visible ray which is 430nm or more as the light source used at this time, and sunrays, a fluorescent lamp, a halogen lamp, the black light, a xenon lamp, a mercury-vapor lamp, a sodium lamp, etc. can be applied.

[0018] The photocatalyst object coating agent of this invention contains titanium oxide and a solvent with the specific ESR spectrum mentioned above. This photocatalyst object coating agent makes it possible to make it easy to cover applying titanium oxide to a building material, automobile material, etc. or a building material, automobile material, etc. with titanium oxide, and to give high photocatalyst activity to a building material, automobile material, etc. As a solvent, an application rear stirrup has the desirable solvent which evaporates after covering and does not remain in titanium oxide, for example, water, a hydrochloric acid, alcohols, and ketones are mentioned.

[0019] This photocatalyst object coating agent can be manufactured by the method of carrying out amalgam decomposition of the method or titanium oxide which water is distributed and slurs the aforementioned titanium oxide from an acid etc. In distribution of titanium oxide, you may carry out by adding a dispersant if needed.

[0020]

[Example] Hereafter, an example explains this invention in detail. In this example, although a photolysis operation of an acetic acid is described, this invention is not limited to this example. In addition, measurement of an ESR spectrum and calculation of g value were performed by the following methods.

[0021] Electron-spin-resonance equipment (a tradename "ESP-300", product made from BRUKER) is used. Temperature : A room temperature, pressure:atmospheric pressure, Microwave Frequency:9.47GHz (=9.47x10⁹s⁻¹), Center Field: 3400G, Sweep Width:500G, Sweep Time: 83.885s, Time Const.:1310.72ms, Mod.Amp. : 5.054G, peak position calculation : It amends with the g value 2.0037 of DPPH. An ESR spectrum is measured by *****, it asks for flux density H (T) in which resonance absorption occurs from the peak of this ESR spectrum, and g value is computed from introducing this flux density into a formula (III). When two or more peaks exist in an ESR spectrum, it asks for flux density about each peak, and g value is computed.

[0022] It hydrolyzed by dropping 146g (a best, product made from the Wako Pure Chem industry) of aqueous ammonia in 20 minutes 25% in a flask, having put in 110g of 10.5N hydrochloric acids of examples, and 25g (a best, product made from the Wako Pure Chem industry) of titanium tetrachlorides into the 300mL flask, having stirred under nitrogen-gas-atmosphere mind, and cooling a flask by iced water. Filtration washing of this hydrolyzate was carried out, and it dried. This dry matter was calcinated in 400-degree C air for 1 hour, and the particle-like titanium oxide (TiO_2) colored yellow was obtained. g value asked for the ESR spectrum of this titanium oxide from an ESR spectrum at drawing 1 is shown in Table 1.

[0023] The glass petri dish with a diameter of 5cm was installed in the direct-vent-system reaction container made from a Pyrex glass (trademark) of the diameter of 8cm, a height of 10cm, and about 0.5 capacity L, and 0.3g of photocatalyst objects which consist only of particle-like titanium oxide obtained on the petri dish in the top was placed. After the volume ratio of oxygen and nitrogen filled the inside of a reaction container with the mixed gas which is 1:4, 33micro mol of acetic acids was enclosed in this container, and the visible ray with a wavelength of 430nm or more was irradiated. It evaluated by measuring with the gas chromatography (a tradename "Column Porapak Q", Shimadzu make) using helium by making into carrier gas concentration of the carbon dioxide which is the oxidative degradation product of the acetic acid which generated the photolysis operation of a photocatalyst object by irradiation of a visible ray. In addition, 500W xenon lamp (a tradename "lamp house UI-502Q, lamp UXL-500D, lighting-device XB-50101 AA-A", USHIO make) equipped with the ultraviolet-rays cut-off filter (a tradename "Y-45", product made from Toshiba glass)

which has the spectral characteristic of drawing 2 was used for the light source. The generation rate of the carbon dioxide at this time was 5.86micromol/h per 1g of photocatalyst objects.

[0024] The photolysis operation of a photocatalyst object was evaluated like the example 1 except having used the photocatalyst object which consists only of titanium oxide (a tradename "ST-01", Ishihara Sangyo make) of example of comparison 1 marketing. The generation rate of the carbon dioxide at this time was 0.46micromol/h per 1g of photocatalyst objects. g value asked for the ESR spectrum of titanium oxide ST-01 from this ESR spectrum at drawing 1 is shown in Table 1.

[0025]

[Table 1]

	実施例 1	比較例 1
g 値	2. 0 2 3 ○ 2. 0 0 5 1. 9 8 5	2. 0 0 3

The thing of O mark shows g value of the maximum peak among Table 1.

[0026] As a result of investigating the visible ray whose wavelength is 430nm or more about the disintegration from an acetic acid to a carbon dioxide on the conditions which irradiate a photocatalyst object, the photocatalyst object of this invention had the high photolysis operation (photocatalyst operation) compared with the photocatalyst object which consists of commercial titanium oxide.

[0027]

[Effect of the Invention] According to this invention, the titanium oxide in which a high photocatalyst operation is shown by irradiation of a visible ray is offered. Moreover, according to this invention, the photocatalyst object containing the titanium oxide in which a high photocatalyst operation is shown by irradiation of a visible ray as a catalyst component can be offered, organic acids, such as an acetic acid, can be begun by using this photocatalyst object, and decomposition removal of the various organic substance can be carried out, and it can also apply to decomposition removal of decomposition removal of the decomposition in [NOx] the atmosphere, the malodorous substance of habitation space or a workspace, mold, etc. or the underwater organic solvent, agricultural chemicals, and Furthermore, according to this invention, by offering the photocatalyst object coating agent containing titanium oxide and a solvent, and using this coating agent, it becomes easy to cover to apply titanium oxide to a building material, automobile material, etc. or a building material, automobile material, etc. with titanium oxide, and a high photocatalyst operation can be given to such material.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The ESR spectrum of the titanium oxide of marketing used in the titanium oxide and the example 1 of comparison which were acquired in the example 1.

[Drawing 2] The wavelength-permeability diagram showing the spectral characteristic of the ultraviolet-rays cut-off filter with which the light source used for the example 1 and the example 1 of comparison was equipped.

[Translation done.]

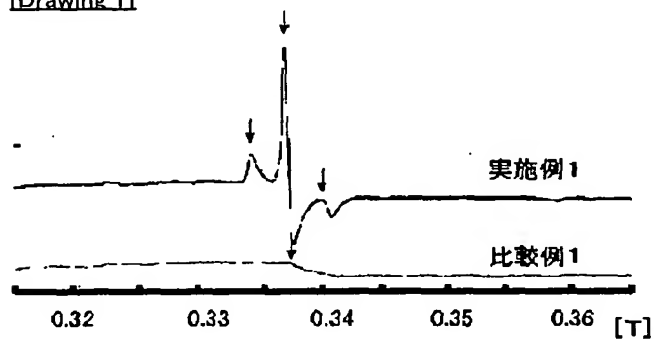
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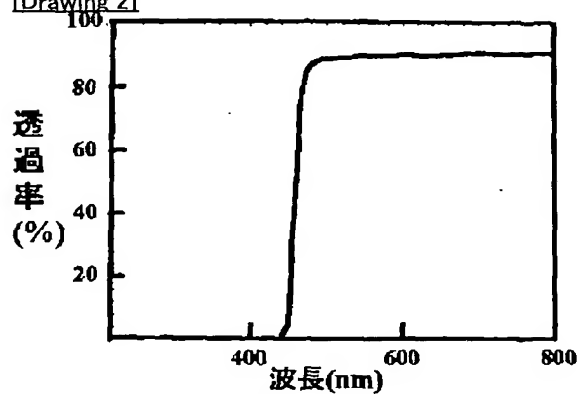
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DRAWINGS

[Drawing 1]



[Drawing 2]



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CORRECTION or AMENDMENT

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102 C

[Procedure revision]

[Filing Date] October 4, Heisei 13 (2001. 10.4)

[Procedure amendment 1]

[Document to be Amended] Specification.

[Item(s) to be Amended] Whole sentence.

[Method of Amendment] Change.

[Proposed Amendment]

[Document Name] Specification.

[Title of the Invention] Titanium oxide.

[Claim(s)]

[Claim 1] Titanium oxide characterized by the peak which has three or more peaks among the g values 1.930-2.030 in an electron-spin-resonance spectrum, and serves as the maximum of these peaks existing among the g values 1.990-2.020.

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to titanium oxide, the photocatalyst object which comes to use it, and a photocatalyst object coating agent. It is related with the titanium oxide as the photocatalyst object in which a high photocatalyst operation is shown by irradiating a visible ray in detail, and its catalyst component, and the photocatalyst object coating agent using it.

[0002]

[Description of the Prior Art] The electron which has a strong reduction operation when ultraviolet rays are irradiated at a semiconductor, and an electron hole with a strong oxidization operation generate, and a oxidation reduction operation decomposes the molecular species in contact with the semiconductor. Decomposition removal of quality of an environmental pollutant, such as decomposition removal of the malodorous substance in the decomposition, the habitation space, and the workspace of NO_x in the atmosphere, mold, etc. or an underwater organic solvent, and agricultural chemicals, a surfactant, can be performed by calling such an operation photocatalyst operation and using this photocatalyst operation. Titanium oxide attracts attention as matter which has a photocatalyst operation, and the photocatalyst object which consists of titanium oxide is marketed. As commercial elegance, there is ST-01 (tradename : Ishihara Sangyo make).

[0003] However, the photocatalyst object which consists of titanium oxide marketed now was not what shows sufficient photocatalyst operation, when irradiating a visible ray.

[0004]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is by irradiating a visible ray to offer

the photocatalyst object in which a high photocatalyst operation is shown, and offer the photocatalyst object coating agent for giving a photocatalyst operation further to the titanium oxide which is the catalyst component and a building material, automobile material, etc.

[0005]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of inquiring wholeheartedly, by irradiating a visible ray, this invention person etc. finds out the titanium oxide as a suitable catalyst component for the photocatalyst object in which a high photocatalyst operation is shown, and came to complete this invention.

[0006] That is, this invention offers the titanium oxide characterized by the peak which has three or more peaks among the g values 1.930–2.030 in an electron-spin-resonance spectrum, and serves as the maximum of these peaks existing among the g values 1.990–2.020.

[0007]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The peak which the titanium oxide of this invention has three or more peaks among the g values 1.930–2.030 in an electron-spin-resonance (henceforth ESR) spectrum, and serves as the maximum of these peaks exists among the g values 1.990–2.020.

[0008] If ESR is divided when the energy ranking of the permanent magnetic dipole of the atom based on an unpaired electron or a molecule adds a magnetic field, and energy equal to the energy between the level is given in the form of electromagnetic energy, electromagnetic energy will be absorbed in resonance and an unpaired electron will say the thing of a phenomenon which causes changes between adjacency *****. ESR analysis investigates the direction of the crystallographic axis of the crystal containing iron family elements, and the property of a chemical bond, and is applied to investigating where [in the molecule] the unpaired electron of the free radical of an organic molecule exists. The crystal structure of titanium oxide was specified in this invention, using as an index g value calculated from ESR analysis.

[0009] With ESR equipment, g value can measure an ESR spectrum and can compute it from the position of the peak of the spectrum. The principle of ESR and the calculation method of g value are as follows [an outline]. If an unpaired electron is placed into a magnetic field, an energy level will be divided by the Zeeman effect. This disunited energy difference is set to ΔE , and it is a lower formula (I).

$$\Delta E = h\nu \quad (I)$$

h expresses a Planck's constant ($=6.6255 \times 10^{-34} \text{Js}$) among [formula (I), and ν expresses Microwave Frequency. When magnetic field strength is changed irradiating the electromagnetic field (frequency ν) of the microwave range to fill, magnetic-field-strength H is a lower formula (II).

$$h\nu = g\beta H \quad (II)$$

In the inside of [formula (II), and g, g value and β express a Bohr magneton ($=9.274 \times 10^{-24} \text{JT}^{-1}$), and H expresses flux density.] Resonance absorption happens at the time of ***** and a peak appears in the resonance absorption curve to which make a horizontal axis into magnetic field strength, and it makes a vertical axis as absorption of electromagnetic field. It is the lower formula (III) to which g value is acquired from the position of this peak as an index showing an unpaired electron's existence state, and g value is led from a formula (II).

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It is alike and asks more. Usually, an ESR spectrum is expressed with the primary differential type of a resonance absorption curve in order to raise detection sensitivity.

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[0012] The titanium oxide with the specific ESR spectrum of this invention can be manufactured by the method of adding a base into the mixture of an acid and a titanium compound for example, under nitrogen-gas-atmosphere mind, and calcinating the obtained product in air etc. As an acid used at this time, a hydrochloric acid, a mineral acid like a sulfuric acid, etc. are mentioned, for example. As a titanium compound, a titanium trichloride, a titanium tetrachloride, sulfuric-acid titanium, titanyl sulfate, etc. are mentioned, for example. As a base, the matter which generates ammonia by ammonia or heating is mentioned, for example. As matter which generates ammonia, a urea, an amide compound like a formamide, an amidine compound like the aceto amidine, a triethanolamine, an amine compound like a hexamethylenetetramine, etc. are mentioned, for example.

[0013] The photocatalyst object of this invention contains titanium oxide with the specific ESR spectrum mentioned above as a catalyst component.

[0014] Although this photocatalyst object consists only for example, of the aforementioned titanium oxide, what applied or covered and was able to obtain titanium oxide to the base material made of the thing of the shape of a sheet acquired by adding a forming assistant to others and particle-like titanium oxide, and carrying out extrusion molding, the thing of the shape of a sheet which was made to carry out the confounding of fibrous titanium oxide and the organic fiber, and was acquired, a metal, or a resin is mentioned. A photocatalyst object may add the inorganic oxide, a macromolecule resin, forming assistants, binders, antistatic agents, or adsorbents other than titanium oxide with the specific ESR spectrum of this invention etc. for the purpose of raising the mechanical strength and a moldability. As an inorganic oxide added by titanium oxide, a silica, an alumina, a zirconia, a magnesia, a zinc oxide, the titanium oxide in which photocatalyst activity is shown by irradiating ultraviolet rays are mentioned, for example.

[0015] What is necessary is to put a photocatalyst object, a processed liquid, or a processed gas into the glass container which penetrates a visible ray on the occasion of use of a photocatalyst object, for example, and just to irradiate the visible ray whose wavelength is 430nm or more at a photocatalyst object using the light source. It is not restricted if wavelength can irradiate a beam of light including the visible ray which is 430nm or more as the light

source used at this time, and sunrays, a fluorescent lamp, a halogen lamp, the black light, a xenon lamp, a mercury-vapor lamp, a sodium lamp, etc. can be applied.

[0016] The photocatalyst object coating agent of this invention contains titanium oxide and a solvent with the specific ESR spectrum mentioned above. This photocatalyst object coating agent makes it possible to make it easy to cover applying titanium oxide to a building material, automobile material, etc. or a building material, automobile material, etc. with titanium oxide, and to give high photocatalyst activity to a building material, automobile material, etc. As a solvent, an application rear stirrup has the desirable solvent which evaporates after covering and does not remain in titanium oxide, for example, water, a hydrochloric acid, alcohols, and ketones are mentioned.

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[0018]

[Example] Hereafter, an example explains this invention in detail. In this example, although a photolysis operation of an acetic acid is described, this invention is not limited to this example. In addition, measurement of an ESR spectrum and calculation of g value were performed by the following methods.

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[0020] Example 1.

0. It hydrolyzed by dropping 146g (a best, product made from the Wako Pure Chem industry) of aqueous ammonia in 20 minutes 25% in a flask, having put in 110g of 5N hydrochloric acids, and 25g (a best, product made from the Wako Pure Chem industry) of titanium tetrachlorides into the 300mL flask, having stirred under nitrogen-gas-atmosphere mind, and cooling a flask by iced water. Filtration washing of this hydrolyzate was carried out, and it dried. This dry matter was calcinated in 400-degree C air for 1 hour, and the particle-like titanium oxide (TiO₂) colored yellow was obtained. g value asked for the ESR spectrum of this titanium oxide from an ESR spectrum at drawing 1 is shown in Table 1.

[0021] The glass petri dish with a diameter of 5cm was installed in the direct-vent-system reaction container made from a Pyrex glass (trademark) of the diameter of 8cm, a height of 10cm, and about 0.5 capacity L, and 0.3g of photocatalyst objects which consist only of particle-like titanium oxide obtained on the petri dish in the top was placed. After the volume ratio of oxygen and nitrogen filled the inside of a reaction container with the mixed gas which is 1:4, 33micro mol of acetic acids was enclosed in this container, and the visible ray with a wavelength of 430nm or more was irradiated. It evaluated by measuring with the gas chromatography (a tradename "Column Porapak Q", Shimadzu make) using helium by making into carrier gas concentration of the carbon dioxide which is the oxidative degradation product of the acetic acid which generated the photolysis operation of a photocatalyst object by irradiation of a visible ray. In addition, 500W xenon lamp (a tradename "lamp house UI-502Q, lamp UXL-500D, lighting-device XB-50101 AA-A", USHIO make) equipped with the ultraviolet-rays cut-off filter (a tradename "Y-45", product made from Toshiba glass) which has the spectral characteristic of drawing 2 was used for the light source. The generation rate of the carbon dioxide at this time was 5.86micromol/h per 1g of photocatalyst objects.

[0022] The example 1 of comparison.

The photolysis operation of a photocatalyst object was evaluated like the example 1 except having used the photocatalyst object which consists only of commercial titanium oxide (a tradename "ST-01", Ishihara Sangyo make). The generation rate of the carbon dioxide at this time was 0.46micromol/h per 1g of photocatalyst objects. g value asked for the ESR spectrum of titanium oxide ST-01 from this ESR spectrum at drawing 1 is shown in Table 1.

[0023]

[Table 1]

	実施例 1	比較例 1
g 値	2. 0 2 3	2. 0 0 3
	○ 2. 0 0 5	
	1. 9 8 5	

The thing of O mark shows g value of the maximum peak among Table 1.

[0024] As a result of investigating the visible ray whose wavelength is 430nm or more about the disintegration from an acetic acid to a carbon dioxide on the conditions which irradiate a photocatalyst object, the photocatalyst object of this invention had the high photolysis operation (photocatalyst operation) compared with the photocatalyst object which consists of commercial titanium oxide.

[0025]

[Effect of the Invention] According to this invention, the titanium oxide in which a high photocatalyst operation is shown by irradiation of a visible ray is offered. Moreover, the thing for which according to this invention the photocatalyst object containing the titanium oxide in which a high photocatalyst operation is shown by irradiation of a visible ray as a catalyst component is offered, and this photocatalyst object is used. Organic acids, such as an acetic acid, can be begun, and decomposition removal of the various organic substance can be carried out, and it can also apply to decomposition removal of decomposition removal of the decomposition in [NOx] the atmosphere, the malodorous substance of habitation space or a workspace, mold, etc. or the underwater organic solvent, agricultural

chemicals, and a surfactant. Furthermore, according to this invention, by offering the photocatalyst object coating agent containing titanium oxide and a solvent, and using this coating agent, it becomes easy to cover to apply titanium oxide to a building material, automobile material, etc. or a building material, automobile material, etc. with titanium oxide, and a high photocatalyst operation can be given to such material.

[Brief Description of the Drawings]

[Drawing 1] The ESR spectrum of the titanium oxide of marketing used in the titanium oxide and the example 1 of comparison which were acquired in the example 1.

[Drawing 2] The wavelength-permeability diagram showing the spectral characteristic of the ultraviolet-rays cut-off filter with which the light source used for the example 1 and the example 1 of comparison was equipped.

[Translation done.]

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(54) 【発明の名称】 酸化チタン、それを用いてなる光触媒体及び光触媒体コーティング剤

(57) 【要約】

【課題】 可視光線を照射することにより高い光触媒作用を示す光触媒体を提供し、さらには、その触媒成分である酸化チタン、及び建築材料、自動車材料等に光触媒作用を付与するための光触媒体コーティング剤を提供する。

【解決手段】 電子スピン共鳴スペクトルにおいて g 値 1.930~2.030 の間に3つ以上のピークを有し、かつそれらピークの内極大となるピークが g 値 1.990~2.020 の間に存在することを特徴とする酸化チタン。

【特許請求の範囲】

【請求項1】 電子スピン共鳴スペクトルにおいてg値1.930～2.030の間に3つ以上のピークを有し、かつそれらピークの内の極大となるピークがg値1.990～2.020の間に存在することを特徴とする酸化チタン。

【請求項2】 触媒成分として請求項1に記載の酸化チタンを含むことを特徴とする光触媒体。

【請求項3】 請求項1に記載の酸化チタンと溶媒とを含むことを特徴とする光触媒体コーティング剤。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は酸化チタン、それを用いてなる光触媒体及び光触媒体コーティング剤に関するものである。詳細には、可視光線を照射することにより高い光触媒作用を示す光触媒体、その触媒成分としての酸化チタン、及びそれを用いた光触媒体コーティング剤に関するものである。

【0002】

【従来の技術】半導体に紫外線を照射すると強い還元作用を持つ電子と強い酸化作用を持つ正孔が生成し、半導体に接触した分子種を酸化還元作用により分解する。このような作用を光触媒作用と呼び、この光触媒作用を利用することによって、大気中のNO_xの分解、居住空間や作業空間での悪臭物質やカビ等の分解除去、あるいは水中の有機溶剤や農薬、界面活性剤等の環境汚染物質の分解除去を行うことができる。光触媒作用を有する物質として酸化チタンが注目され、酸化チタンからなる光触媒体が市販されている。市販品として、例えば、ST-01（商品名：石原産業製）がある。

【0003】しかしながら、現在市販されている酸化チタンからなる光触媒体は、可視光線を照射する場合には十分な光触媒作用を示すものではなかった。

【0004】

【発明が解決しようとする課題】本発明の課題は、可視光線を照射することにより高い光触媒作用を示す光触媒体を提供し、さらには、その触媒成分である酸化チタン、及び建築材料、自動車材料等に光触媒作用を付与するための光触媒体コーティング剤を提供することにある。

【0005】

【課題を解決するための手段】本発明者等は上記課題を解決するため鋭意検討を行った結果、可視光線を照射することにより高い光触媒作用を示す光触媒体に好適な触媒成分としての酸化チタンを見出し、本発明を完成するに至った。

【0006】すなわち本発明は、電子スピン共鳴スペクトルにおいてg値1.930～2.030の間に3つ以上のピークを有し、かつそれらピークの内の極大となるピークがg値1.990～2.020の間に存在するこ

とを特徴とする酸化チタンを提供するものである。

【0007】また本発明は、触媒成分として前記の酸化チタンを含むことを特徴とする光触媒体を提供するものである。

【0008】さらに本発明は、前記の酸化チタンと溶媒とを含むことを特徴とする光触媒体コーティング剤を提供するものである。

【0009】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明の酸化チタンは、電子スピン共鳴（以下、ESRという。）スペクトルにおいてg値1.930～2.030の間に3つ以上のピークを有し、かつそれらピークの内の極大となるピークがg値1.990～2.020の間に存在するものである。

【0010】ESRとは、不対電子に基づく原子ないし分子の永久磁気双極子のエネルギー順位が磁場を加えることにより分裂し、その準位間のエネルギーに等しいエネルギーを電磁エネルギーの形で与えると、共鳴的に電磁エネルギーを吸収して不対電子は相隣る準位間で遷移を起こす現象のことをいう。ESR分析は、例えば、鉄族元素を含む結晶の結晶軸の方向及び化学結合の性質を調べたり、また有機分子の遊離基の不対電子がその分子中のどこに存在するかを調べることに応用されている。本発明では、ESR分析から求められるg値を指標として用い酸化チタンの結晶構造を特定した。

【0011】g値は、ESR装置でESRスペクトルを測定し、そのスペクトルのピークの位置から算出することができる。ESRの原理およびg値の算出方法は概略以下のとおりである。不対電子が磁場の中に置かれると、ゼーマン効果によりエネルギー準位が分裂する。この分裂したエネルギー差を ΔE とし、下式（I）

$$\Delta E = h\nu \quad (I)$$

〔式（I）中、hはプランク定数（ $=6.6255 \times 10^{-34} \text{ J s}$ ）、 ν はMicrowave Frequencyを表す。〕を満たすマイクロ波領域の電磁場（周波数 ν ）を照射しながら磁場の強さを変化させていくと、磁場の強さHが下式（II）
$$h\nu = g\beta H \quad (II)$$

〔式（II）中、gはg値、 β はボーア磁子（ $=9.274 \times 10^{-24} \text{ J T}^{-1}$ ）、Hは磁束密度を表す。〕を満たすときに共鳴吸収が起こり、横軸を磁場の強さ、縦軸を電磁場の吸収とする共鳴吸収曲線にピークが現れる。このピークの位置から不対電子の存在状態を表す指標としてg値が得られ、g値は式（II）から導かれる下式（III）

$$g = h\nu / (\beta H) \quad (III)$$

により求められる。通常、ESRスペクトルは、検出感度を向上させる為、共鳴吸収曲線の一次微分形で表される。

【0012】特定のESRスペクトルをもつ酸化チタンが何故、可視光線の照射により優れた光触媒活性を発現

し得るか明らかではないが、Journal of the Physical Chemistry, 89, 5689-5694 (1985)によれば、このESRスペクトルにおけるg値1.930~2.030の間のピークは窒素(原子量14)を含むラジカル種に由来すると思われることから、窒素の存在及びその存在に起因する酸化チタンの結晶格子内に生じる歪みが酸化チタンの光触媒活性に影響を及ぼしていると考えられる。

【0013】酸化チタンは、例えば、粒子、繊維状のような各種形状のものが挙げられ、使用方法に応じて適当な形状が選定される。また、酸化チタンは、可視光線の照射による光触媒活性を損なわない範囲で、無機化合物が混合されたものであってもよいし、また無機化合物が混合された後、熱処理等が施されて無機化合物と複合化されたものであってもよい。酸化チタンに混合される無機化合物としては、例えば、シリカ(SiO_2)、アルミナ(Al_2O_3)、ジルコニア(ZrO_2)、マグネシア(MgO)、酸化亜鉛(ZnO)等が挙げられる。

【0014】本発明の特定のESRスペクトルをもつ酸化チタンは、例えば、窒素雰囲気下で酸とチタン化合物との混合物に塩基を添加し、得られた生成物を空气中で焼成する方法等により製造することができる。このときに用いる酸としては、例えば、塩酸、硫酸のような鉱酸等が挙げられる。チタン化合物としては、例えば、三塩化チタン、四塩化チタン、硫酸チタン、硫酸チタニル等が挙げられる。塩基としては、例えば、アンモニア又は加熱によりアンモニアを生成する物質が挙げられる。アンモニアを生成する物質としては、例えば、尿素、ホルムアミドのようなアミド化合物、アセトアミジンのようなアミジン化合物、トリエタノールアミン、ヘキサメチレンテトラミンのようなアミン化合物等が挙げられる。

【0015】本発明の光触媒は、触媒成分として上述した特定のESRスペクトルをもつ酸化チタンを含む。

【0016】この光触媒は、例えば、前記酸化チタンだけからなるもののほか、粒子状の酸化チタンに成形助剤を添加し押出成形して得られたシート状のもの、繊維状の酸化チタンと有機繊維とを交絡させて得られたシート状のもの、又は金属若しくは樹脂製の支持体に酸化チタンを塗布又は被覆して得られたもの等が挙げられる。光触媒は、その機械的強度、成形性を向上させることを目的に、本発明の特定のESRスペクトルをもつ酸化チタン以外の無機酸化物、高分子樹脂、成形助剤、結合剤、帯電防止剤又は吸着剤等を添加したものであってもよい。酸化チタンに添加される無機酸化物としては、例えば、シリカ、アルミナ、ジルコニア、マグネシア、酸化亜鉛、紫外線を照射することにより光触媒活性を示す酸化チタン等が挙げられる。

【0017】光触媒の使用に際しては、例えば、可視光線を透過するガラス製容器に光触媒と被処理液又は被処理気体とを入れ、光源を用いて光触媒に波長が430nm以上である可視光線を照射すればよい。このと

き用いる光源としては、波長が430nm以上である可視光線を含む光線を照射できるものであれば制限されるものではなく、例えば、太陽光線、蛍光灯、ハロゲンランプ、ブラックライト、キセノンランプ、水銀灯、ナトリウムランプ等が適用できる。

【0018】本発明の光触媒コーティング剤は、上述した特定のESRスペクトルをもつ酸化チタンと溶媒とを含む。この光触媒コーティング剤は、建築材料、自動車材料等に酸化チタンを塗布すること、又は建築材料、自動車材料等を酸化チタンで被覆することを容易にし、かつ建築材料、自動車材料等に高い光触媒活性を付与することを可能とする。溶媒としては、塗布後又は被覆後に蒸発して酸化チタンに残存しない溶媒が好ましく、例えば、水、塩酸、アルコール類、ケトン類等が挙げられる。

【0019】この光触媒コーティング剤は、例えば、前記の酸化チタンを水に分散させてスラリー化する方法又は酸化チタンを酸等で溶解させる方法等で製造することができる。酸化チタンの分散では、必要に応じて分散剤を添加し行ってもよい。

【0020】

【実施例】以下、本発明を実施例により詳細に説明する。本実施例では、酢酸の光分解作用について述べるが、本発明は本実施例に限定されるものではない。なお、ESRスペクトルの測定及びg値の算出は、以下の方法で行った。

【0021】電子スピン共鳴装置(商品名“ESP-300”、BRUKER製)を用い、温度：室温、圧力：大気圧、Microwave Frequency：9.47GHz(=9.47×10⁹s⁻¹)、Center Field：3400G、Sweep Width：500G、Sweep Time：83.885s、Time Const.：1310.72ms、Mod. Amp.：5.054G、ピーク位置算出：DPPHのg値2.0037で補正、の条件でESRスペクトルを測定し、このESRスペクトルのピークから共鳴吸収が起きる磁束密度H

(T)を求め、この磁束密度を式(III)に導入することより、g値を算出する。ESRスペクトルに複数のピークが存在するときは、それぞれのピークについて磁束密度を求め、g値を算出する。

【0022】実施例1

0.5N塩酸110gと四塩化チタン(特級、和光純薬工業製)25gを300mLフラスコ中に入れ、窒素雰囲気下で攪拌し、フラスコを氷水で冷却しながら、フラスコ内に25%アンモニア水(特級、和光純薬工業製)146gを20分間で滴下し加水分解を行った。この加水分解物を戸洗浄し乾燥した。この乾燥物を400℃の空气中で1時間焼成して、黄色に着色した粒子状酸化チタン(TiO_2)を得た。この酸化チタンのESRスペクトルを図1に、ESRスペクトルから求められるg値を表1に示す。

【0023】直径8cm、高さ10cm、容量約0.5Lのバイレックスガラス（商標）製密閉式反応容器内に直径5cmのガラス製シャーレを設置し、そのシャーレ上に上で得られた粒子状酸化チタンだけからなる光触媒体0.3gを置いた。反応容器内を、酸素と窒素の体積比が1:4である混合ガスで満たした後、該容器内に酢酸33 μmol を封入し、波長430nm以上の可視光線を照射した。光触媒体の光分解作用を、可視光線の照射により生成した酢酸の酸化分解生成物である二酸化炭素の濃度をキャリアーガスとしてヘリウムを用いたガスクロマトグラフィー（商品名“カラムPorapak Q”、島津製作所製）で測定することによって、評価した。尚、光源には、図2の分光特性を有する紫外線カットフィルター（商品名“Y-45”、東芝硝子製）を装着した500Wキセノンランプ（商品名“ランプハウスUI-502Q、ランプUXL-500D、点灯装置XB-50101AA-A”、ウシオ電機製）を用いた。このときの二酸化炭素の生成速度は光触媒体1gあたり5.86 $\mu\text{mol/h}$ であった。

【0024】比較例1

市販の酸化チタン（商品名“ST-01”、石原産業製）だけからなる光触媒体を用いた以外は、実施例1と同様にして光触媒体の光分解作用を評価した。このときの二酸化炭素の生成速度は光触媒体1gあたり0.46 $\mu\text{mol/h}$ であった。酸化チタンST-01のESRスペクトルを図1に、このESRスペクトルから求められたg値を表1に示す。

【0025】

【表1】

	実施例1	比較例1
g 値	2.023 ○2.005 1.985	2.003

【図1】

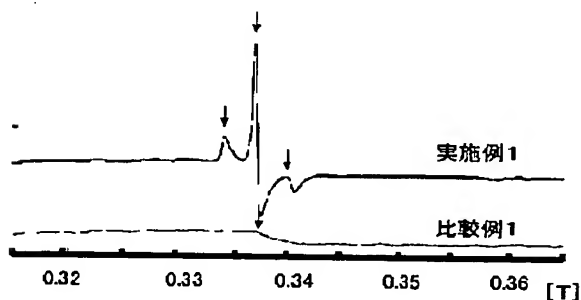


表1中、○印のものは極大ピークのg値を示す。

【0026】波長が430nm以上である可視光線を光触媒体に照射する条件で、酢酸から二酸化炭素への分解作用について調べた結果、本発明の光触媒体は市販の酸化チタンからなる光触媒体に比べて、光分解作用（光触媒作用）が高かった。

【0027】

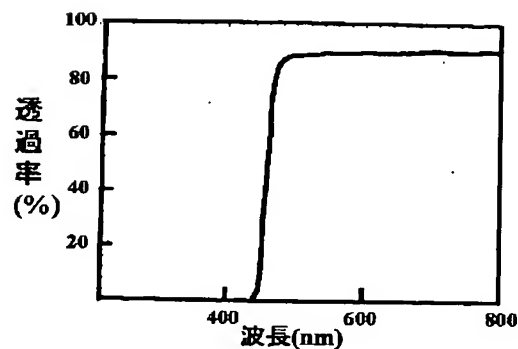
【発明の効果】本発明によれば、可視光線の照射によって高い光触媒作用を示す酸化チタンが提供される。また本発明によれば、触媒成分として可視光線の照射により高い光触媒作用を示す酸化チタンを含む光触媒体が提供され、この光触媒体を使用することによって酢酸等の有機酸をはじめ各種有機物を分解除去することができ、また、大気中NO_xの分解、居住空間や作業空間の悪臭物質、カビ等の分解除去、あるいは水中の有機溶剤、農薬、界面活性剤の分解除去に適用することもできる。さらに本発明によれば、酸化チタンと溶媒とを含む光触媒体コーティング剤が提供され、このコーティング剤を使用することによって、建築材料、自動車材料等に酸化チタンを塗布すること、又は建築材料、自動車材料等を酸化チタンで被覆することが容易になり、これらの材料に高い光触媒作用を付与することができる。

【図面の簡単な説明】

【図1】 実施例1で得られた酸化チタン及び比較例1で使用した市販の酸化チタンのESRスペクトル。

【図2】 実施例1、比較例1に用いた光源に装着した紫外線カットフィルターの分光特性を示す波長-透過率線図。

【図2】



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